Different Radiation Grafted Ion-exchange Membranes for Polymer Electrolyte Fuel Cell

Tanja Kallio[a], Matts Lundström[a], Göran Sundholm[a],
Nadia Walsby[b], Franciska Sundholm[b]
[a]Helsinki University of Technology
[b]University of Helsinki
[a]Laboratory of Physical Chemistry and Electrochemistry,
PB 6100, FIN-02015 HUT, FINLAND
[b]Laboratory of Polymer Chemistry,
PB 55, FIN-00014 HY, FINLAND

Radiation grafting has been widely used to produce proton conducting membranes for polymer electrolyte fuel cells (PEFC). Typically, a pre-formed fluorine containing polymer film is irradiated, subsequently grafted and finally sulfonated. Advantages of this method are low preparation costs, a high degree of control over the process and the possibility to use pre-processed films. In order to determine the influence of the matrix material on the membrane, a series of membranes based on different fluoropolymers were prepared under similar conditions, resulting in membranes with comparable degrees of grafting (30…40 %).[1]

The conductivities of the membranes increased with decreasing crystallinity and thus with increasing water uptake. Thin membranes had lower conductivities than thick membranes, however, the area resistances of the former are lower than latter, suggesting that thinner membranes will give better performances in the fuel cell. Conductivity increased with temperature in the range 20…70°C, obeying approximately the Arrhenius equation. At 60°C all radiation-grafted membranes had conductivities comparable to those of Nafion® 105 and 117. See also "Influence of the initial fluoropolymer in polystyrene sulfonic acid containing radiation-grafted membranes" by N. Walsby *et al.*

Reactant gas permeabilities were measured with chronoamperometric method in a microelectrode cell. No major differences in permeabilities or fluxes of oxygen and hydrogen at temperature of 20°C and about 100 % relative humidity were detected. The hydrogen flux appeared to be several times higher than that of oxygen. The reactant gas fluxes in the radiation-grafted membranes appeared to be similar to those in Nafion® 105 but slightly higher than for Nafion® 117.

As expected the thinner membranes had better performances in the fuel cell (60°C, atmospheric pressure). Nevertheless, the membranes with the best conductivities appeared to be less durable in the fuel cell. The reason for this was crack formation caused by a high mechanical stress due to uneven swelling and shrinking of the membrane at the border of the active and the inactive area.

The reactant gas permeabilities appear not to depend on the properties of the matrix material. Instead they affect conductivity and durability under the fuel cell conditions. Apparently, in the choice of host material a compromise has to be done between the last two properties.

[1]Walsby, N., Sundholm, F., Kallio, T., Sundholm, G., J. Polym. Sci. Part A: Polym. Chem., submitted.

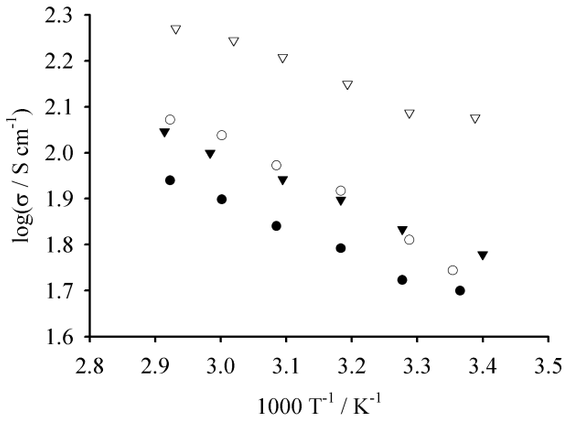

Figure 1. Conductivity as a function of temperature (100 % RH). (●) PVDFa-g-PSSA, (▼) PVDF-co-HFP(6%)-g-PSSA, (▽)PVDF-co-HFP(15%)-g-PSSA and (○) Nafion® 105.

Table 1. Oxygen permeabilities at 20°C and 100 % RH.

matrix	10^6 D $cm^2\ s^{-1}$	10^6 c mol cm^{-3}	d (wet) μm	10^9 Dc/d mol $cm^{-2}\ s^{-1}$
PVDFa	6.2	3.2	130	1.7
PVDFb	6.1	2.8	70	2.4
PVDF-co-HFP(6%)	6.3	2.0	130	1.1
PVDF-co-HFP(15%)	8.5	3.8	120	2.7
FEP	8.9	1.3	145	1.3
ETFE	6.4	1.9	90	2.1
Nafion® 105	8.0	6.1	150	4.1
Nafion® 117	1.1	9.3	210	0.50

Table 2. Hydrogen permeabilities at 20°C and 100 % RH.

matrix	10^6 D $cm^2\ s^{-1}$	10^6 c mol cm^{-3}	10^9 Dc/d mol $cm^{-2}\ s^{-1}$
PVDFa	9.2	5.0	4.6
PVDFb	5.6	8.6	6.9
PVDF-co-HFP(6%)	12	4.7	5.0
PVDF-co-HFP(15%)	5.7	9.1	4.3
FEP	11	8.5	11
ETFE	9.1	4.2	6.4
Nafion® 105	11	2.2	6.3
Nafion® 117	17	7.0	1.9